The equivalent and aliovalent dopants boosting the thermoelectric properties of YbMg_2Sb_2

Xinxin Yang¹, Yayun Gu¹, Yuping Li¹, Kai Guo^{1*}, Jiye Zhang^{1*} and Jing-Tai Zhao^{1,2}

ABSTRACT Antimony-based Zintl compounds AM_2Sb_2 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}, \text{Yb}, \text{Eu}$; $\text{M}=\text{Mg}, \text{Zn}, \text{Cd}, \text{Mn}$), which enable a broad range of manipulation on electrical and thermal transport properties, are considered as an important class of thermoelectric materials. Phonon and carrier transport engineering were realized in YbMg_2Sb_2 via equivalent and aliovalent substitution of Zn and Ag, respectively. The room-temperature thermal conductivity reduces from 1.96 to $1.15 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$ due to the mass and strain fluctuation through the formation of the absolute solid solution of YbMg_2Sb_2 - YbZn_2Sb_2 . Furthermore, the carrier concentration has been further optimized by Ag doping (from 0.42×10^{19} to $7.72 \times 10^{19} \text{ cm}^{-3}$ at room temperature), and thus the electrical conductivity and the power factor are enhanced effectively. The integrated aspects make the dimensionless figure of merit (zT) reach 0.48 at 703 K, which is 60% higher than the pristine YbMgZnSb_2 sample.

Keywords: Zintl phase, YbMg_2Sb_2 , solid solution, thermal conductivity, thermoelectric properties

INTRODUCTION

Recent global energy and environmental crisis prompt researchers to seek renewable and reliable energy resources, as well as novel strategies to utilize the waste energy in the surrounding environment. Thermoelectrics, as a clean and sustainable energy technology, enabling a direct conversion between heat and electricity based on the Seebeck and Peltier effect [1–3]. The conversion efficiency of a thermoelectric (TE) material is determined by the dimensionless figure of merit $zT = \sigma S^2 T / (\kappa_L + \kappa_e)$, where σ , S , T , κ_L and κ_e represent the electrical conductivity, Seebeck coefficient, absolute temperature, and the lattice and electronic components of thermal conductivity κ , respectively. For a highly efficient TE mate-

rial, a combination of high σ , large S and low κ are fundamentally required. However, σ , S and κ are strongly coupled in nature, which makes it difficult to optimize one single property without vitiating the others [4–7].

Zintl compounds, AM_2Sb_2 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}, \text{Yb}, \text{Eu}$; $\text{M}=\text{Mg}, \text{Zn}, \text{Cd}, \text{Mn}$) with a CaAl_2Si_2 -type structure (space group $P\bar{3}m1$), are considered as one class of potential TE materials [8–14]. Normally, p-type AM_2Sb_2 compounds show appealing TE properties owing to their low thermal conductivity derived from the strong lattice anharmonicity and moderate electrical transport properties [9]. Enhancement of TE properties for typical p-type AM_2Sb_2 can be realized by regulating the doping at both A and M sites [15]. Gascoin *et al.* [16] reported that alloying Ca at the Yb site in YbZn_2Sb_2 would simultaneously reduce the carrier concentration and the thermal conductivity. In addition, Zevalkink *et al.* [17] demonstrated that the carrier concentration could be optimized through the Yb vacancies in $\text{Yb}_{1-\delta}\text{Zn}_2\text{Sb}_2$. Zhang *et al.* [18] proposed orbital alignment to increase the band degeneracy and thus improve the power factor in 122-type Zintl compounds, which was confirmed in YbCd_2Sb_2 - YbZn_2Sb_2 system [19]. Recently, Mg-containing compounds with the same structure exhibit impressive TE performance including Mg_3Sb_2 [20,21], $\text{Ca}_{1-x}\text{Yb}_x\text{Mg}_2\text{Bi}_2$ [22] and $\text{CaMg}_{2-x}\text{Zn}_x\text{Sb}_2$ [23], while YbMg_2Sb_2 has rarely been focused as TE material so far.

In this work, the YbMg_2Sb_2 - YbZn_2Sb_2 system was investigated to obtain possible band alignment and suppressed thermal conductivity. Subsequently, aliovalent Ag ion doping was carried out with the aim to optimize the hole concentration for maximizing the power factor. Eventually, Mg/Zn substitution results in the reduction of the thermal conductivity to $0.73 \text{ W m}^{-1} \text{ K}^{-1}$ at 573 K, and the power factor increases to $7.58 \text{ mW cm}^{-1} \text{ K}^{-2}$ at 703 K

¹ School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

² State Key Laboratory of Advanced Special Steel, Shanghai University, Shanghai 200444, China

* Corresponding authors (emails: kai.guo@shu.edu.cn (Guo K); jy Zhang@shu.edu.cn (Zhang J))

by doping Ag. As a result, a promising zT value of 0.48 is achieved at 703 K in the sample of $\text{Yb}(\text{MgZn})_{0.992}\text{Ag}_{0.008}\text{Sb}_2$.

EXPERIMENTAL SECTION

Polycrystalline $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$ ($x=0, 0.5, 1, 1.5, 2$) and $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$ ($y=0, 0.002, 0.004, 0.006, 0.008$) samples were synthesized by element combination reaction. The raw materials (Yb 99.9%, Mg 99.99%, Zn 99.999%, Ag 99.999%, Sb 99.999%) were weighed in a glove box (M. Braun, $\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm) according to stoichiometric ratio, and then transferred into BN crucibles sealed in evacuated fused quartz tubes using a Partulab device (MRVS-3002). The reactants were slowly heated to 1273 K at a rate of 1 K/min and kept for 3 days. Subsequently, these assemblies were cooled to room temperature by switching off the furnace. The products were thoroughly ground and annealed at 873 K for another 7 days for homogenization. The as-obtained samples were sintered using a vacuum hot-press furnace at 773 K for 30 min with a pressure of 70 MPa to obtain sufficiently dense bulk samples.

The phase purities of the as-prepared samples were examined by powder X-ray diffraction (PXRD, Rigaku, Cu K α radiation, $\lambda=1.541854$ Å, $10^\circ < 2\theta < 80^\circ$, step width 0.02°) at room temperature. The cell parameters were obtained by means of WinCSD software [24]. The microstructure and composition were characterized by using a scanning electron microscope (SEM; ZEISS Gemini 300, Germany) equipped with energy-dispersive X-ray spectroscopy (EDX; Oxford X-MAX, UK). The Seebeck coefficient and conductivity of the samples were measured by using a ZEM-3 apparatus (ULVAC-RIKO, Japan) under a helium atmosphere from room temperature to 703 K. Hall effect measurements were performed under the applied magnetic field of ~ 1 to 1 T in a Hall Characterization System (LINSEIS, L79/HCS, Germany) at room temperature. The thermal conductivity was calculated according to $\kappa_{\text{tot}}=C_p\lambda d$, where λ is the thermal diffusivity, C_p is the specific heat capacity, and d is the density. The λ of a disk sample with a diameter of 10 mm and a typical thickness of 1–2 mm was measured using laser flash diffusivity (NETZSCH, LFA457, Germany). Prior to measurement, the sample was coated with a thin graphite layer to minimize the error in material emissivity. C_p was determined using the Dulong-Petit approximation. d was measured at room temperature by applying the Archimedes method.

RESULTS AND DISCUSSION

The crystal structure of trigonal YbMg_2Sb_2 can be seen elsewhere [25]. This compound belongs to CaAl_2Si_2 -structure type [26], which is derived from a layered stacking of anionic framework and cationic layers along the c axis. In the anionic framework, each Mg atom is connected with four Sb atoms to form MgSb_4 tetrahedral, which are connected each other by sharing vertices and edges. Cations of Yb are positioned between the anionic layers to provide the electrons for satisfying the charge balance. Fig. 1a shows the PXRD patterns of the as-synthesized polycrystalline $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$ ($x=0, 0.5, 1, 1.5, 2$). The simulated pattern of the YbZn_2Sb_2 (ICSD No. 380377) is also provided for comparison. Apparently, the as-obtained polycrystalline samples can be indexed as YbZn_2Sb_2 phase despite obvious angle-shifts, indicating that YbMg_2Sb_2 and YbZn_2Sb_2 can form absolute solid solution. With increasing x , all diffraction peaks shift towards higher angle, revealing the lattice shrinkage derived from smaller atomic radius of Zn (Fig. 1b). As expected, the lattice parameters a and c both linearly decrease with the increasing Zn content, following the Vegard's law. Temperature dependent thermal conductivities for $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$ ($0 \leq x \leq 2$) are shown in Fig. 1c. The total thermal conductivity continuously decreases as temperature increases, evidencing a dominant phonon scattering by Umklapp processes. The total thermal conductivity tends to decrease first and then increase with rising x at the measured temperature range (Fig. 1d), which can be understood from the alloying effect. Zn alloying Mg would induce the mass and strain fluctuation, and thus the minimum thermal conductivity can be observed with $x=1$. The electronic thermal conductivity increases with increasing Zn content, since YbZn_2Sb_2 has high electrical conductivity in comparison with YbMg_2Sb_2 (Fig. 1e). The lattice thermal conductivity exhibits a minimum value with $x=1$ as the total thermal conductivity (Fig. 1f). However, a high orbital degeneracy at the valence band maximum to maximum the power factor has not been achieved in this work (Supplementary information, Fig. S1), probably due to the larger composition gap.

Since the disorder of Mg and Zn would result in strong phonon scattering and enable to achieve the minimum thermal conductivity for the series samples $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$, the sample YbMgZnSb_2 was further manipulated to increase the TE figure of merit zT , where the substitution of Ag at Mg/Zn site was performed to optimize the carrier concentration. Fig. 2 displays the PXRD patterns for $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$ ($y \leq 0.008$). All

Figure 1 PXRD patterns for the $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$ samples (a), the cell parameters of the $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$ samples (b), temperature-dependent total thermal conductivity (c), composition-dependent total thermal conductivity at 300 and 573 K (d), electronic (e) and lattice thermal conductivity (f) for $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$ ($0 \leq x \leq 2$).

the main diffraction peaks can be indexed as YbZn_2Sb_2 phase as well. In comparison to YbMgZnSb_2 , the reflection peaks of Ag-substituted samples slightly shifted toward lower angle with increasing x , revealing the lattice expansion behavior. Several additional weak peaks, such as Sb_2O_5 and Sb (marked in Fig. 2), were observed from the traces of the impurity phase, which may be caused by oxygen impurities in the reactants and loss of Mg caused by volatilization during the synthesized process.

The Hall carrier concentration (n_H) for $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$ (Fig. 3a) increases linearly with increasing y ($y \leq 0.008$). Ag substitution at Mg/Zn site can introduce more holes, and successfully rise carrier concentration from $0.42 \times 10^{19} \text{ cm}^{-3}$ in pristine YbMgZnSb_2

up to $7.72 \times 10^{19} \text{ cm}^{-3}$ in $\text{Yb}(\text{MgZn})_{0.992}\text{Ag}_{0.008}\text{Sb}_2$ at room temperature. Compared with the theoretical value, the experimental carrier concentration is slightly higher due to the inherent defects of the Zintl compounds [27]. Besides, the loss of Mg at high temperature caused by volatilization can also lead to a higher carrier concentration. In general, the increased carrier concentration may cause a reduction of the mobility to a certain degree. However, a substantially constant mobility has been observed in Fig. 3b.

The backscattered electron images of typical YbMgZnSb_2 and $\text{Yb}(\text{MgZn})_{0.992}\text{Ag}_{0.008}\text{Sb}_2$ samples are presented in Fig. 4a and b, respectively. Dense surface and homogeneous composition can be identified for the two

Figure 2 PXRD patterns for the $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$ samples.

samples. EDX mapping was performed on the composition of the sample $\text{Yb}(\text{MgZn})_{0.992}\text{Ag}_{0.008}\text{Sb}_2$ (Fig. 4d–g). Elements Yb, Mg, Zn, Sb, and Ag are homogeneously distributed, which is consistent with the high purity of the sample determined by PXRD analysis.

The temperature dependences of electrical conductivity, Seebeck coefficient and power factor for $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$ are shown in Fig. 5a–c. The electrical conductivity of the pristine sample decreases below 528 K and then increases until 703 K, which results from the intrinsic excitation behavior of semiconductor YbMgZnSb_2 . For the Ag-doped samples, electrical conductivity linearly decreases with increasing temperature, indicating heavily doped degenerate semiconductor behavior. Importantly, the electrical conductivity improves from 0.24×10^4 to $4.45 \times 10^4 \text{ S m}^{-1}$ at 303 K and from $0.27 \times$

10^4 to $2.65 \times 10^4 \text{ S m}^{-1}$ at 703 K as a result of Ag doping. The profound improvement in electrical conductivity is ascribed to the increasing carrier concentration, as shown in Fig. 3a.

The Seebeck coefficients of all the samples are positive, evidencing a p-type conduction behavior, which is consistent with the Hall coefficient measurements (Fig. 3). In addition, the Seebeck coefficient of undoped sample YbMgZnSb_2 decreases at higher temperature due to the intrinsic excitation of carriers (bipolar diffusion). The peak of Seebeck coefficient curve is utilized for evaluating the band gap ($E_g = 2eS_{\text{max}}T_{\text{max}}$) value of 0.66 eV [28]. After Ag doping, the monotonically increased Seebeck coefficient is attributed to the rising intrinsic excitation temperature, resulting in the suppression effect of heavily doped bipolar diffusion. Fig. 6 shows the Pisarenko plot at room temperature for $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$ [16,19,25,29–32]. All the experimental data plots fall nearly perfectly on the fitting line of $m^* = 0.7m_0$ (m_0 is the mass of a free electron, $m^* = 0.5m_0$ and $m^* = 1m_0$ are shown for comparison), revealing that the valence band structure remains almost unchanged after Ag doping. The as-obtained effective masses for $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$ are in good agreement with the values of other 122 Zintl phases. Although Seebeck coefficient decreases with Ag doping, there is a significant enhancement in the power factor (from 2.75 to $7.58 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 703 K), which is mainly attributed to the increase in electrical conductivity.

The temperature dependences of total thermal conductivities are shown in Fig. 5d. The thermal conductivity continues to decrease linearly from 303 to 703 K, representing a typical crystalline heat transport behavior. Despite the fact that the total thermal conductivity continuously increases with Ag content increasing, the highest thermal conductivity component of

Figure 3 Room-temperature carrier concentration (a), and Hall mobility of $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$ ($0 \leq y \leq 0.008$).

Figure 4 SEM images of YbMgZnSb₂ (a) and Yb(MgZn)_{0.992}Ag_{0.008}Sb₂ (b), and EDX mapping images corresponding to the rectangular area of Yb(MgZn)_{0.992}Ag_{0.008}Sb₂ (c–g).

Yb(MgZn)_{0.992}Ag_{0.008}Sb₂ ($1.70 \text{ W m}^{-1} \text{ K}^{-1}$) is still lower than that of YbMg₂Sb₂ ($1.96 \text{ W m}^{-1} \text{ K}^{-1}$) and YbZn₂Sb₂ ($3.25 \text{ W m}^{-1} \text{ K}^{-1}$) at 303 K. The electrical thermal conductivity increases continuously with increasing y (Fig. 5e), which is calculated using the Wiedemann-Franz law ($\kappa_e = L\sigma T$, L is the Lorenz factor determined from the classic single parabolic band (SPB) model with acoustic scattering). The increase in total thermal conductivity is mainly due to the increase of electronic thermal conductivity. The lattice thermal conductivity gradually decreases with the increasing temperature, basically conforming to the function of T^{-1} , revealing a dominant phonon scattering at higher temperature (Fig. 5f). Simultaneously, the lattice thermal conductivity decreases slightly as rising x due to point defect scattering attributed to the size and the atom mass fluctuation among Mg, Zn and Ag.

Although the Ag-doping slightly increases the thermal conductivity, it contributes more to the electrical prop-

Figure 5 Temperature dependence of electrical conductivity (a), Seebeck coefficient (b), power factor (c), total (d), electrical (e) and lattice thermal conductivity (f) for Yb(MgZn)_{1-y}Ag_ySb₂.

Figure 6 Seebeck coefficient as function of Hall carrier concentration for $\text{Yb}(\text{Mg}_{1-x}\text{Zn}_x)_{1-y}\text{Ag}_y\text{Sb}_2$. The corresponding data for CaZn_2Sb_2 [16,25], EuZn_2Sb_2 [9,29,30], EuCd_2Sb_2 [31] and YbCd_2Sb_2 [19,32] are provided for comparison.

Figure 7 Temperature dependence of figure of merit zT for $\text{Yb}(\text{MgZn})_{1-y}\text{Ag}_y\text{Sb}_2$.

erties and eventually reaches a maximum $zT=0.48$ at 703 K for $\text{Yb}(\text{MgZn})_{0.992}\text{Ag}_{0.008}\text{Sb}_2$ (Fig. 7), which has an obvious improvement 60% higher than $\text{Yb}(\text{MgZn})\text{Sb}_2$ ($zT=0.3$). From the trend of the curve, even higher zT are expected to be further achieved above 703 K.

CONCLUSIONS

Polycrystalline $\text{Yb}(\text{Mg}_{1-x}\text{Zn}_x)_{1-y}\text{Ag}_y\text{Sb}_2$ ($0 \leq x \leq 2$, $0 \leq y \leq 0.008$) samples were prepared by the traditional solid-state reaction followed by vacuum hot-pressing sintering technology. The room-temperature thermal conductivity is reduced from 1.96 to 1.15 $\text{W m}^{-1} \text{K}^{-1}$ by solid solution

of YbMg_2Sb_2 and YbZn_2Sb_2 . Furthermore, the carrier concentration is optimized (from 0.42×10^{19} to $7.72 \times 10^{19} \text{ cm}^{-3}$ at room temperature) by the doping of Ag, thereby improving the electrical conductivity and the power factor. The combination of the two aspects makes zT reach 0.48 at 703 K, which is 60% higher than that of the pure sample YbMgZnSb_2 . This work gives a good understanding of the TE compound YbMg_2Sb_2 , and also provides a valuable idea for improving the TE properties of YbM_2Sb_2 solid solution.

Received 19 July 2019; accepted 25 September 2019;
published online 7 November 2019

- 1 Tritt TM. Thermoelectric materials: Holey and unholey semiconductors. *Science*, 1999, 283: 804–805
- 2 Zhang X, Zhao LD. Thermoelectric materials: Energy conversion between heat and electricity. *J Materiomics*, 2015, 1: 92–105
- 3 DiSalvo FJ. Thermoelectric cooling and power generation. *Science*, 1999, 285: 703–706
- 4 Zhang Q, Sun Y, Xu W, *et al.* Organic thermoelectric materials: Emerging green energy materials converting heat to electricity directly and efficiently. *Adv Mater*, 2014, 26: 6829–6851
- 5 Toberer ES, May AF, Snyder GJ. Zintl chemistry for designing high efficiency thermoelectric materials. *Chem Mater*, 2010, 22: 624–634
- 6 Dresselhaus M, Chen G, Tang M, *et al.* New directions for low-dimensional thermoelectric materials. *Adv Mater*, 2017, 19: 1043–1053
- 7 Wei TR, Qin Y, Deng T, *et al.* Copper chalcogenide thermoelectric materials. *Sci China Mater*, 2019, 62: 8–24
- 8 Cao QG, Zhang H, Tang MB, *et al.* Zintl phase $\text{Yb}_{1-x}\text{Ca}_x\text{Cd}_2\text{Sb}_2$ with tunable thermoelectric properties induced by cation substitution. *J Appl Phys*, 2010, 107: 053714
- 9 Guo K, Cao Q, Zhao J. Zintl phase compounds AM_2Sb_2 ($A=\text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}, \text{Yb}$; $M=\text{Zn}, \text{Cd}$) and their substitution variants: A class of potential thermoelectric materials. *J Rare Earths*, 2013, 31: 1029–1038
- 10 Wang X, Li W, Wang C, *et al.* Single parabolic band transport in p-type EuZn_2Sb_2 thermoelectrics. *J Mater Chem A*, 2017, 5: 24185–24192
- 11 Toberer ES, May AF, Melot BC, *et al.* Electronic structure and transport in thermoelectric compounds AZn_2Sb_2 ($A=\text{Sr}, \text{Ca}, \text{Yb}, \text{Eu}$). *Dalton Trans*, 2010, 39: 1046–1054
- 12 Guo K, Cao QG, Feng XJ, *et al.* Enhanced thermoelectric figure of merit of Zintl phase $\text{YbCd}_{2-x}\text{Mn}_x\text{Sb}_2$ by chemical substitution. *Eur J Inorg Chem*, 2011, 2011(26): 4043–4048
- 13 Shuai J, Mao J, Song S, *et al.* Recent progress and future challenges on thermoelectric Zintl materials. *Mater Today Phys*, 2017, 1: 74–95
- 14 Shuai J, Geng H, Lan Y, *et al.* Higher thermoelectric performance of Zintl phases $(\text{Eu}_{0.5}\text{Yb}_{0.5})_{1-x}\text{Ca}_x\text{Mg}_2\text{Bi}_2$ by band engineering and strain fluctuation. *Proc Natl Acad Sci USA*, 2016, 113: E4125–E4132
- 15 Takagiwa Y, Sato Y, Zevalkink A, *et al.* Thermoelectric properties of EuZn_2Sb_2 Zintl compounds: zT enhancement through Yb substitution for Eu. *J Alloys Compd*, 2017, 703: 73–79
- 16 Gascoin F, Ottensmann S, Stark D, *et al.* Zintl phases as thermo-

- electric materials: Tuned transport properties of the compounds $\text{Ca}_x\text{Yb}_{1-x}\text{Zn}_2\text{Sb}_2$. *Adv Funct Mater*, 2005, 15: 1860–1864
- 17 Zevalkink A, Zeier WG, Cheng E, *et al.* Nonstoichiometry in the Zintl Phase $\text{Yb}_{1-\delta}\text{Zn}_2\text{Sb}_2$ as a route to thermoelectric optimization. *Chem Mater*, 2014, 26: 5710–5717
 - 18 Zhang J, Song L, Pedersen SH, *et al.* Discovery of high-performance low-cost n-type Mg_3Sb_2 -based thermoelectric materials with multi-valley conduction bands. *Nat Commun*, 2017, 8: 13901
 - 19 Wang XJ, Tang MB, Chen HH, *et al.* Synthesis and high thermoelectric efficiency of Zintl phase $\text{YbCd}_{2-x}\text{Zn}_x\text{Sb}_2$. *Appl Phys Lett*, 2009, 94: 092106
 - 20 Ohno S, Imasato K, Anand S, *et al.* Phase boundary mapping to obtain n-type Mg_3Sb_2 -based thermoelectrics. *Joule*, 2018, 2: 141–154
 - 21 Song L, Zhang J, Iversen BB. Simultaneous improvement of power factor and thermal conductivity *via* Ag doping in p-type Mg_3Sb_2 thermoelectric materials. *J Mater Chem A*, 2017, 5: 4932–4939
 - 22 Shuai J, Liu Z, Kim HS, *et al.* Thermoelectric properties of Bi-based Zintl compounds $\text{Ca}_{1-x}\text{Yb}_x\text{Mg}_2\text{Bi}_2$. *J Mater Chem A*, 2016, 4: 4312–4320
 - 23 Wood M, Aydemir U, Ohno S, *et al.* Observation of valence band crossing: The thermoelectric properties of CaZn_2Sb_2 - CaMg_2Sb_2 solid solution. *J Mater Chem A*, 2018, 6: 9437–9444
 - 24 Akselrud L, Grin Y. WinCSD: Software package for crystallographic calculations (Version 4). *J Appl Crystallogr*, 2014, 47: 803–805
 - 25 Mewis A. AB_2X_2 -Verbindungen im CaAl_2Si_2 -Typ, IV[1] Zur Struktur der Verbindungen CaZn_2Sb_2 , CaCd_2Sb_2 , SrZn_2Sb_2 und SrCd_2Sb_2 / AB_2X_2 Compounds with the CaAl_2Si_2 Structure, IV[1] The Crystal Structure of CaZn_2Sb_2 , CaCd_2Sb_2 , SrZn_2Sb_2 , and SrCd_2Sb_2 . In: *Zeitschrift für Naturforschung B*, 1978, 382
 - 26 Burdett JK, Miller GJ. Fragment formalism in main-group solids: Applications to aluminum boride (AlB_2), calcium aluminum silicide (CaAl_2Si_2), barium-aluminum (BaAl_4), and related materials. *Chem Mater*, 1990, 2: 12–26
 - 27 Pomrehn GS, Zevalkink A, Zeier WG, *et al.* Defect-controlled electronic properties in AZn_2Sb_2 zintl phases. *Angew Chem Int Ed*, 2014, 53: 3422–3426
 - 28 Goldsmid HJ, Sharp JW. Estimation of the thermal band gap of a semiconductor from seebeck measurements. *J Elec Materi*, 1999, 28: 869–872
 - 29 Klüfers P, Neumann H, Mewis A, *et al.* AB_2X_2 -Verbindungen im CaAl_2Si_2 -Typ, VIII[1]/ AB_2X_2 Compounds with the CaAl_2Si_2 Structure, VIII[1]. In: *Zeitschrift für Naturforschung B*, 1980, 1317
 - 30 Zhang H, Zhao JT, Grin Y, *et al.* A new type of thermoelectric material, EuZn_2Sb_2 . *J Chem Phys*, 2008, 129: 164713
 - 31 Zheng L, Li W, Wang X, *et al.* Alloying for orbital alignment enables thermoelectric enhancement of EuCd_2Sb_2 . *J Mater Chem A*, 2019, 7: 12773–12778
 - 32 Artmann A, Mewis A, Roepke M, *et al.* AM_2X_2 -verbindungen mit CaAl_2Si_2 -struktur. XI. Struktur und eigenschaften der verbindungen ACd_2X_2 (A: Eu, Yb; X: P, As, Sb). *Z Anorg Allg Chem*, 1996, 622: 679–682

Acknowledgements This work was supported by the National Key Research and Development Program of China (2018YFA0702100), the National Natural Science Foundation of China (21771123), the Programme of Introducing Talents of Discipline to Universities (D16002), the Science and Technology Commission of Shanghai Municipality (15DZ2260300), and Key Laboratory of Optoelectronic Materials

Chemistry and Physics, Chinese Academy of Sciences (2008DP173016).

Author contributions Yang X wrote this manuscript with the support from Li Y and Zhao J-T. Guo K designed the experiments and analyzed the data. Gu Y performed the experiments. Zhang J did the property measurements. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Xinxin Yang received her Bachelor's degree from Central South University in 1999, and PhD degree from Shanghai Institute of Ceramics, Chinese Academy of Sciences under the supervision of Prof. Jing-Tai Zhao in 2013. Her research interest focuses on the crystal structure and physical properties of intermetallic compounds.

Kai Guo received his Bachelor's degree from Huazhong University of Science and Technology in 2006, and PhD from Shanghai Institute of Ceramics, Chinese Academy of Sciences under the supervision of Prof. Jing-Tai Zhao in 2011. He worked on high-pressure synthesis as a postdoctor in Max-Planck Institute for Chemical Physics of solids. His research interest focuses on the structure-property relationship of thermoelectric materials.

Jiye Zhang obtained his PhD degree from the Institute of Physics, Chinese Academy of Sciences in 2008. Now, he is an associate professor of the School of Materials Science and Engineering, Shanghai University. His main research interests focus on exotic thermal and electrical transport behaviors in thermoelectric materials from the interplay among spin, charge and lattice of degrees of freedom.

通过等价和异价元素掺杂促进 YbMg_2Sb_2 热电性能提升

杨昕昕¹, 顾亚运¹, 李玉瓶¹, 郭凯^{1*}, 张继业^{1*}, 赵景泰^{1,2}

摘要 由于其电热输运性能便于调控, 锑基Zintl相化合物 AM_2Sb_2 (A=Ca, Sr, Ba, Yb, Eu; M=Mg, Zn, Cd, Mn)被认为是一类重要的热电材料. 本文通过在 YbMg_2Sb_2 中掺入等价的元素Zn和异价元素Ag, 实现了声子和载流子的输运性能优化. 首先, 体系 $\text{YbMg}_{2-x}\text{Zn}_x\text{Sb}_2$ 室温热导率从 $1.96 \text{ W m}^{-1} \text{ K}^{-1}$ 降低至 $1.15 \text{ W m}^{-1} \text{ K}^{-1}$, 这是由于形成 YbMg_2Sb_2 - YbZn_2Sb_2 的固溶体带来的合金化散射效应. 其次, 掺杂Ag可以增加载流子浓度, 其数值在室温下从 $0.42 \times 10^{19} \text{ cm}^{-3}$ 提升至 $7.72 \times 10^{19} \text{ cm}^{-3}$, 从而有效地提高了电导率和功率因子. 通过综合两方面的协同效应使得体系 zT 在703 K时达到0.48, 比纯样品 YbMgZnSb_2 高60%.